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Structure of (1R)-1,8,8-Trimethyl-3-oxabicyclo[3.2.1]octane-2,4-dione (Camphoric Anhydride)

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Abstract. $C_{10}H_{14}O_3$, $M_r = 182 \cdot 22$, orthorhombic, $P2_12_12_1$, $a = 6 \cdot 486$ (1), $b = 11 \cdot 203$ (2), $c = 13 \cdot 027$ (2) Å, $V = 946 \cdot 6$ Å^3, $Z = 4$, $D_x = 1 \cdot 278$ (1) Mg m^{-3}, λ(Cu $K\alpha$) $= 1 \cdot 5418$ Å, μ(Cu $K\alpha$) $= 0 \cdot 778$ mm^{-1}, $F(000) = 392$, $T = 290$ (1) K, $R = 0 \cdot 034$ for 905 observed independent reflections. The six-membered ring shows a half-boat conformation with marked non-planarity of the anhydride moiety.

Introduction. Knowledge of the ring geometry is indispensable for interpretation of the NMR spectra of glutaric anhydrides (Koer, de Hoog & Altona, 1975). The existence of large differences among ring torsion angles points to the strong influence of the substituents on the conformation of these compounds (Hašek, 1985). Changes of the ring and chromophore geometry are responsible for the strong substituent and solvent dependence of circular dichroism (CD) spectra of cyclic anhydrides. Interesting examples of this are the camphoric acid derivatives with a bicyclic skeleton for which the CD curves are strongly solvent dependent (Połoński, 1983). The structure of the bicyclic title compound was required for the analysis of its CD spectrum.

Experimental. Crystals of the title compound were grown from toluene. Unit-cell parameters were determined from oscillation and Weissenberg photographs, which showed orthorhombic symmetry with systematic absences $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd, indicating space group $P2_12_12_1$. A needle-like crystal of dimensions $0 \cdot 75 \times 0 \cdot 25 \times 0 \cdot 20$ mm was used for data collection on a Stoe automatic four-circle diffractometer. Accurate cell parameters were obtained from a least-squares fit of θ values for 43 high-order reflections. The following data collection regime was applied: ω–2θ scan, 55 steps of $0 \cdot 2°$, count time per step $0 \cdot 3$–$1 \cdot 8$ s, $\theta_{max} = 60°$ ($0 \le h \le 7$, $0 \le k \le 12$, $0 \le l \le 14$), two standard intensities ($00\bar{6}$ and 040) were checked every 90 min with no significant variation of their intensities. 926 unique reflections were measured of which 21 with $I < 2\sigma(I)$ were treated as unobserved in subsequent calculations. Lorentz and polarization but no absorption corrections were applied.

The structure was solved by direct methods and refined by full-matrix least squares using the *XTAL* package of programs (Stewart & Hall, 1983) on a VAX computer. The correct enantiomer was chosen on the basis of the known chirality of natural camphor, from which the compound was synthesized. H-atom positions were taken from a difference Fourier map and refined individually with isotropic temperature factors. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Minimized function $\sum w(F_o - F_c)^2$, with final values of $R = 0 \cdot 034$ and $wR = 0 \cdot 033$; $w = 1/\sigma^2(F)$. Ratio of maximum parameter shift to e.s.d. in the last cycle of refinement was $0 \cdot 02$ for non-hydrogen atoms and $0 \cdot 05$

for hydrogens. Maximum and minimum heights in final $\Delta\rho$ map were 0·15 and −0·17 e Å⁻³. The final atomic coordinates are listed in Table 1.*

Discussion. The bond lengths and angles are listed in Table 2. The molecular structure is shown with the atom numbering scheme in Fig. 1 and unit-cell contents are shown in Fig. 2.

All bond lengths agree well with standard values for corresponding bond types in glutaric anhydrides of known structure: bromovalerone anhydride (Hoehne, 1966); *β*-chloroglutaric anhydride (Koer *et al.*, 1975); *meso*-2,4-dimethylglutaric anhydride (Haltiwanger, Walba & Wand, 1980); *erythro*-2-methoxymethyl-2,4-dimethylglutaric anhydride (Hašek, 1985); α-phenylglutaric anhydride (Bocelli & Grenier-Loustalot, 1982)

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43516 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and 1-oxacyclohexane-4-spirocyclopentane-2,6-dione (Bocelli, Grenier-Loustalot & Urbanczyk-Lipkowska, 1982). Bonds between C and H atoms (which were refined without constraints) have lengths in the region 0·96–1·09 Å.

The six-membered ring shows a half-boat conformation; following the Cremer & Pople (1975) notation, the values of the ring-puckering parameters are Q = 0·630 (5) Å, θ = 46·0 (6)° and φ = 2·6 (7)°. Atoms C(7) and O(1) lie correspondingly 0·89 (1) Å above and 0·13 (1) Å below the plane formed by C(1), C(2), C(3) and C(4) atoms. Carbonyl oxygens O(2) and O(3) are above this plane [0·09 (1) and 0·02 (1) Å respectively]. The striking feature of this conformation is the distinct non-planarity of the anhydride group as a result of the geometric constraints followed from the bicyclic structure of the compound. The bridging atom C(7) is a member of both five- and six-membered rings and the angle C(1)–C(7)–C(4) = 99·2 (2)° is far from the standard value indicated for the above-mentioned glutaric anhydrides (about 110°) and is typical for compounds with bicyclo[2.2.1]heptane (Bear & Trotter, 1975; Połoński & Dauter, 1986) and bicyclo-[3.2.1]octane skeletons (Cheer, Martz, Harpp & Friedlander, 1985). None of the intermolecular distances are shorter than the sum of van der Waals radii. The

Table 1. *Final positional parameters* (×10⁴) *and equivalent isotropic thermal parameters* (×10²) *for non-hydrogen atoms with their e.s.d.'s in parentheses*

U_{eq} is defined according to Hamilton (1959).

	x	y	z	U_{eq}(Å²)
C(1)	823 (5)	−281 (2)	252 (2)	4·58
O(1)	4102 (3)	784 (2)	553 (2)	5·34
C(2)	3050 (5)	−71 (3)	−12 (2)	5·12
O(2)	4010 (4)	−537 (2)	−688 (2)	8·24
C(3)	3325 (5)	1260 (3)	1456 (2)	5·05
O(3)	4462 (4)	1873 (2)	1942 (2)	7·52
C(4)	1128 (4)	980 (2)	1685 (2)	4·48
C(5)	−213 (5)	1692 (3)	918 (3)	5·81
C(6)	−351 (5)	889 (3)	−27 (2)	5·63
C(7)	667 (4)	−336 (2)	1436 (2)	4·24
C(8)	2183 (5)	−1206 (3)	1937 (3)	5·62
C(9)	−1532 (5)	−648 (4)	1793 (3)	6·08
C(10)	23 (7)	−1373 (4)	−326 (3)	7·38

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·503 (4)	C(3)—O(3)	1·189 (4)
C(1)—C(6)	1·559 (4)	C(3)—C(4)	1·490 (4)
C(1)—C(7)	1·547 (3)	C(4)—C(5)	1·546 (4)
C(1)—C(10)	1·527 (5)	C(4)—C(7)	1·539 (4)
O(1)—C(2)	1·387 (4)	C(5)—C(6)	1·527 (5)
O(1)—C(3)	1·388 (4)	C(7)—C(8)	1·530 (4)
C(2)—O(2)	1·198 (4)	C(7)—C(9)	1·541 (4)

C(2)—C(1)—C(6)	106·5 (2)	O(3)—C(3)—C(4)	127·5 (3)
C(2)—C(1)—C(7)	107·3 (2)	C(3)—C(4)—C(5)	107·5 (2)
C(2)—C(1)—C(10)	109·9 (3)	C(3)—C(4)—C(7)	110·2 (2)
C(6)—C(1)—C(7)	103·5 (2)	C(5)—C(4)—C(7)	104·4 (2)
C(6)—C(1)—C(10)	113·1 (3)	C(4)—C(5)—C(6)	104·5 (3)
C(7)—C(1)—C(10)	115·9 (3)	C(1)—C(6)—C(5)	106·2 (3)
C(2)—O(1)—C(3)	122·5 (2)	C(1)—C(7)—C(4)	99·2 (2)
C(1)—C(2)—O(1)	117·4 (2)	C(1)—C(7)—C(8)	114·1 (2)
C(1)—C(2)—O(2)	126·8 (3)	C(1)—C(7)—C(9)	111·8 (3)
O(1)—C(2)—O(2)	115·8 (3)	C(4)—C(7)—C(8)	113·3 (2)
O(1)—C(3)—O(3)	116·6 (3)	C(4)—C(7)—C(9)	109·5 (3)
O(1)—C(3)—C(4)	115·8 (2)	C(8)—C(7)—C(9)	108·8 (3)

Fig. 1. Perspective view of the molecule.

Fig. 2. View of the molecules within the unit cell.

additional factor contributing to the non-planarity of the O=C—O—C=O group is probably the repulsion between the methyl at C(7) and the O(1) atom.

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Benzyl-9 Diméthyl-5,8 Diméthylamino-3 Carbazolecarbaldéhyde-4*

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Abstract. $C_{24}H_{24}N_2O$, $M_r = 356 \cdot 5$, triclinic, $P\bar{1}$, $a = 13 \cdot 205$ (4), $b = 9 \cdot 553$ (3), $c = 8 \cdot 556$ (1) Å, $\alpha = 104 \cdot 35$ (2), $\beta = 110 \cdot 11$ (2), $\gamma = 98 \cdot 09$ (3)°, $V = 951 \cdot 2$ Å³, $D_m = 1 \cdot 27$, $D_x = 1 \cdot 24$ Mg m⁻³, $Z = 2$, λ(Mo $K\alpha$) = $0 \cdot 7107$ Å, $\mu = 0 \cdot 071$ mm⁻¹, $F(000) = 380$, room temperature, $R = 0 \cdot 037$ for 2663 independent reflections $[I > 3\sigma(I)]$. The carbazole group is not as planar as it is in the carbazole molecule. This distortion is due to steric hindrance. The phenyl ring of the benzyl group and the pyrrole ring are almost perpendicular. The structure can be regarded as consisting either of layers of molecules which are spread out along the (100) planes or of columns built around the [010] axes.

Introduction. La synthèse de la diméthylamino-9 ellipticine par la méthode de Pomeranz (1893) et

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* La numérotation utilisée dans le titre est différente de celle indiquée sur la Fig. 1 et utilisée dans le reste de ce mémoire.

Fritsch (1893) conduit à préparer, comme produit intermédiaire, le diméthyl-1,4 diméthylamino-6 carbazolecarbaldéhyde-3. Selon que la formylation, par la méthode de Vilsmeier & Haack (1927), est réalisée sur le diméthyl-1,4 diméthylamino-6 carbazole ou sur son analogue méthoxylé en 6, le groupement CHO se fixe exclusivement en 9 ou de façon prépondérante en 3. La formylation du produit obtenu après blocage de l'azote carbazolique en 9 par le groupement benzyle paraissait donc susceptible de fournir un dérivé formylé en 3. En fait, on obtient un mélange de composés mono et diformylé qui ont été séparés par chromatographie. Par suite de la présence de pics supplémentaires dus aux atomes d'hydrogène aromatiques du groupement benzyle, les spectres de RMN à 250 MHz n'ont pas permis de connaître les positions occupées par le nouveau substituant. C'est la raison pour laquelle l'étude cristallographique a été entreprise. Des cristaux du composé monoformylé ont été obtenus par évaporation